

MARINE SURFACTANT CHEMISTRY

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LONG-TERM GOAL

Sea-surface films modify the boundary conditions affecting important air-sea interfacial processes accessible by remote sensing. These processes include exchange of momentum and mass, bubble and foam stabilization, aerosol formation, and the absorbance and scattering of electromagnetic radiation. The overall goals of this research are to relate the surface properties of natural sea-surface films to their chemical composition and to predict the probable range of surface viscoelasticity for different ocean provinces.

SCIENTIFIC OBJECTIVES

The scientific objectives are:

1. Determine sources and molecular composition of organic matter in the surface microlayer; and
2. Understand how changing molecular composition of microlayers affects viscoelastic response and its impact on sea surface roughness.

APPROACH

Surface microlayers and underlying bulk seawater are collected using a rotating glass skimmer for varying sea surface conditions, including unslicked surfaces, diffuse slick regions, and strongly banded slicks. Surfactants are isolated either by foam tower enrichment (adsorption on bubble surfaces) followed by solvent extraction, or by solid phase adsorption followed by solvent elution of the adsorbed surfactants. Mass spectrometry is used to determine chemical composition. Fragmentation patterns are acquired by pyrolysis-mass spectrometry (PyMS) for analysis by multiple regression techniques. Static and dynamic surface properties of these fractions are correlated with molecular composition and molecular structure. A quantitative description of microlayer films covering different dynamic and physical conditions in a variety of geographic and productivity regimes is developed.

WORK COMPLETED

Completed works include:

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1. Linear discriminant analysis (LDA) has been applied to mass spectral data derived from microlayer and bulk surface seawater surfactant organic matter. The LDA used a two-step principal component analysis to find mass descriptors that maximized the between-sample variance. The LDA results have been correlated with static surface elasticities measured for surface films of these materials; and
2. A new benchtop ion trap mass spectrometer, purchased with DURIP funding, has been installed and evaluated for its utility in analyzing complex microlayer surfactant mixtures.

RESULTS

Significant variations in microlayer composition are observed spatially due to changing organic matter composition in the underlying bulk water. The contribution from colored humic materials, for example, decreases strongly with distance from estuarine and terrestrial sources. Wind stress and subsurface water motions also play a strong role in controlling enrichment of the major surfactant classes that dominate microlayer surface elasticity. The resulting mixture of surfactant types determines the air-sea interfacial elasticity. This is best illustrated with an example using microlayers collected in the mid-Atlantic and southern California Bights (Figures 1-3). In Figure 1, typical mass spectra of three hexane/methylene chloride-extracted surfactant mixtures from (1) a surface bulk water sample, (2) an unslicked microlayer, and (3) a strongly slicked microlayer are presented. The spectrum of the bulk seawater sample is dominated by intense ions from only a few compounds, whose structures we have shown to be poloxamers (mixed ethylene oxide/propylene oxide polymers) of unknown origin. In the spectrum of the visibly unslicked microlayer, additional low intensity ions are observed in the 80-150, 200-300, and 350-470 m/z regions, representing the presence of small amounts of adsorbed lipid materials, primarily free and bound fatty acids, steroids, and terpenoids, along with the poloxamers. The spectrum of the third sample indicates that these components, seen in minor amounts in the unslicked microlayer, are heavily enriched in the slicked microlayer relative to the poloxamers.

The effect of this changing composition on interfacial elasticity is shown in Figure 2, in which measured static surface elasticities (ϵ) are plotted as a function of film surface pressure (π) for the same three samples. Our measurements of poloxamers isolated and purified from natural seawater have been shown that these compounds have intrinsically low elasticity at a given surface pressure; this is reflected in the $\epsilon-\pi$ plot for the bulk water surfactants in Figure 2. Increasing adsorption of the lipoidal surfactants have a strong effect in increasing ϵ (up to a factor of 4).

The mass spectra therefore may be expected to contain information not only about chemical composition, but also the surface elasticity. This hypothesis was tested by applying a multivariate analysis technique (LDA) to the mass spectra of a suite of 16 microlayer and bulk seawater samples. Discriminant functions were developed that distinguished each sample spectrum from every other based on the spectra. The discriminant functions were evaluated for each spectrum to provide a discriminant score. Experimentally measured static elasticities for the samples were then compared with the discriminant scores to determine the degree of correlation between composition and surface elasticity. It was found that elasticities were strongly correlated with the scores of the first ranked discriminant, D1 and that the mass spectra contained sufficient information to predict film elasticities to within 20% using only D1 scores. The predicted and observed elasticities for this 16 sample suite are compared in Figure 3. The slope of the linear fit

(dashed line) is very close to the 1:1 relationship plotted as a solid line. Deviations from the 1:1 line are predominantly due to the fact that only D1 was used in the prediction, thus ignoring information in lower ranked discriminants. A similar analysis (along with other multivariate techniques) is being applied to a larger data set to test the generality of this approach.

IMPACT/APPLICATION

A method for relating the composition and molecular structure of complex natural surface films to interfacial physical properties has been demonstrated. The PyMS-LDA method combines chemical and structural data with statistical analysis. The advantage of this approach is that it facilitates identification of the end-member components in complex mixtures that determine the elasticity of microlayer films. The mass spectra of microlayer organics can be used to predict elasticity from the spectra. This approach could be applied to *in situ* mapping of slick composition and surface elasticity by coupling our recently acquired benchtop mass spectrometer, which is capable of detecting and measuring individual film components in unresolved mixtures using multistage MS (Ms^n), with a microlayer sampler.

RELATED PROJECTS

This project has relevance to those ONR-funded projects investigating (1) oceanic and atmospheric processes that modulate small scale waves and air-sea fluxes and (2) remote sensing imagery of the ocean surface using passive and active microwave sensors.

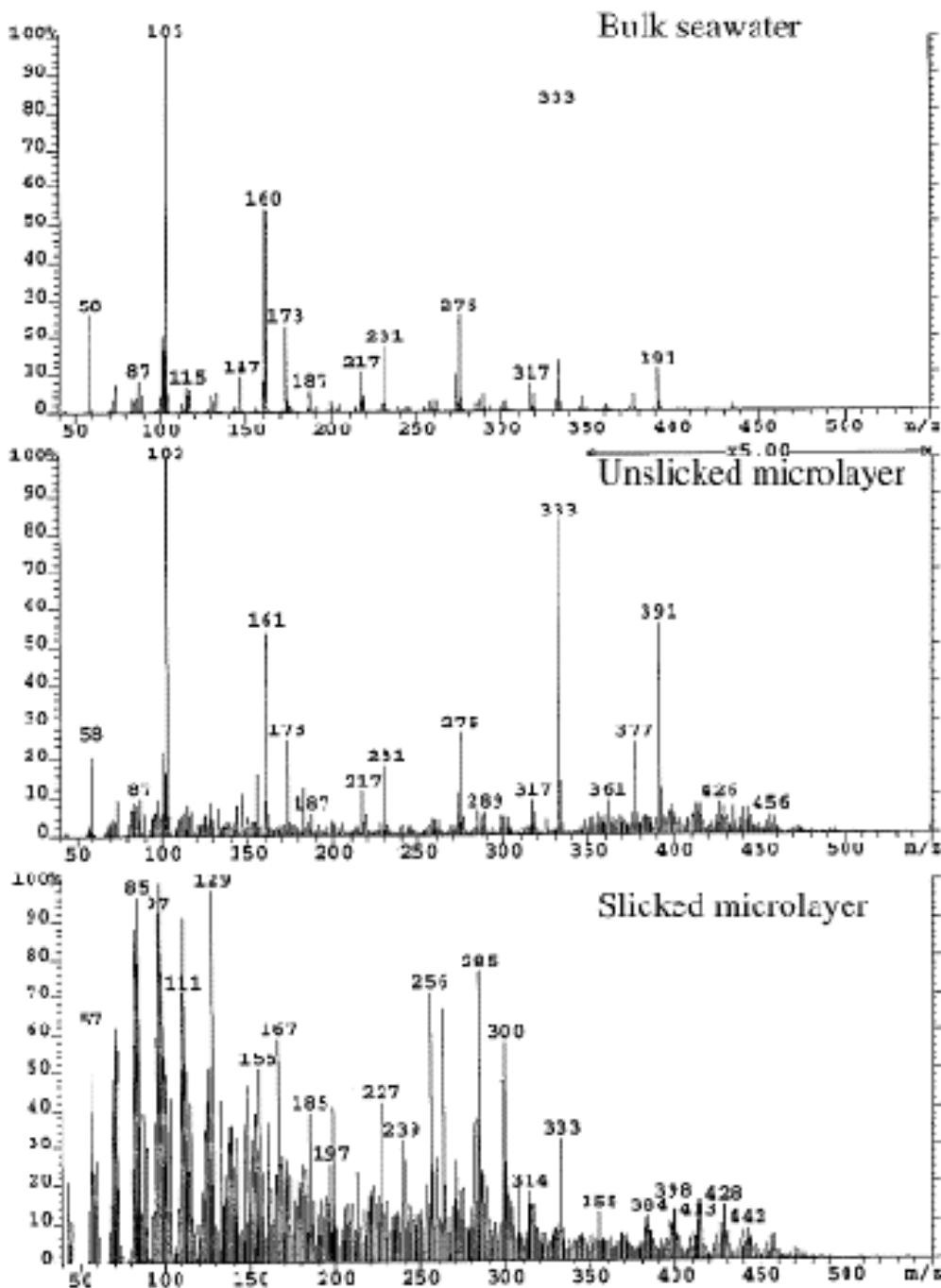


Figure 1. Mass Spectra of Hexane/Methylene Chloride Extractable Surfactants in Bulk Surface Seawater (Upper), Unslicked Surface Microlayer (Center) and Slicked Microlayer (Lower). Spectra Shows Dominance of Poloxamer Components in Bulk Water and Increasing Enrichments of More Hydrophobic Lipoidal Surfactants in the Microlayers.

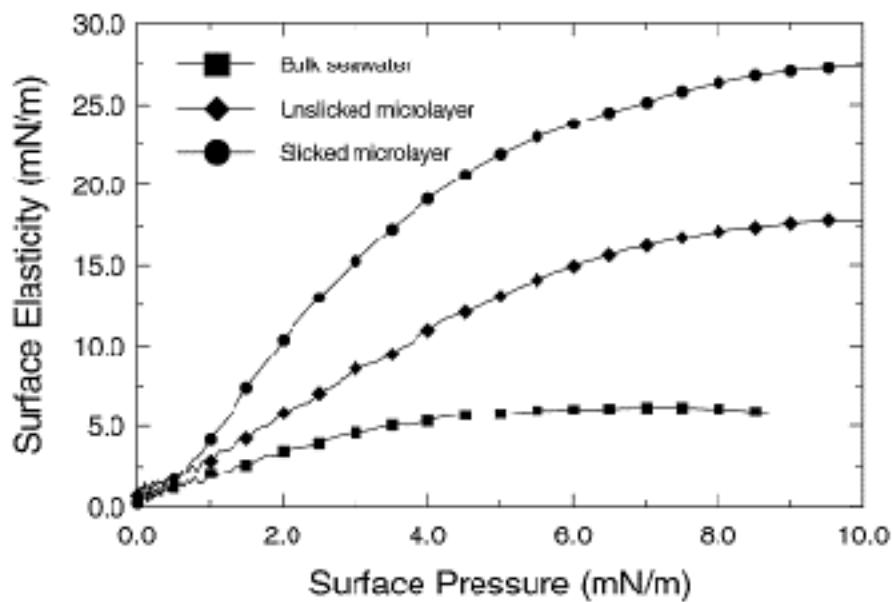


Figure 2. Variation of Elasticity with Surface Pressure of Films Corresponding to the Compositions shown in Figure 1. Highest Elasticities are Observed for Films with High Lipid Content.

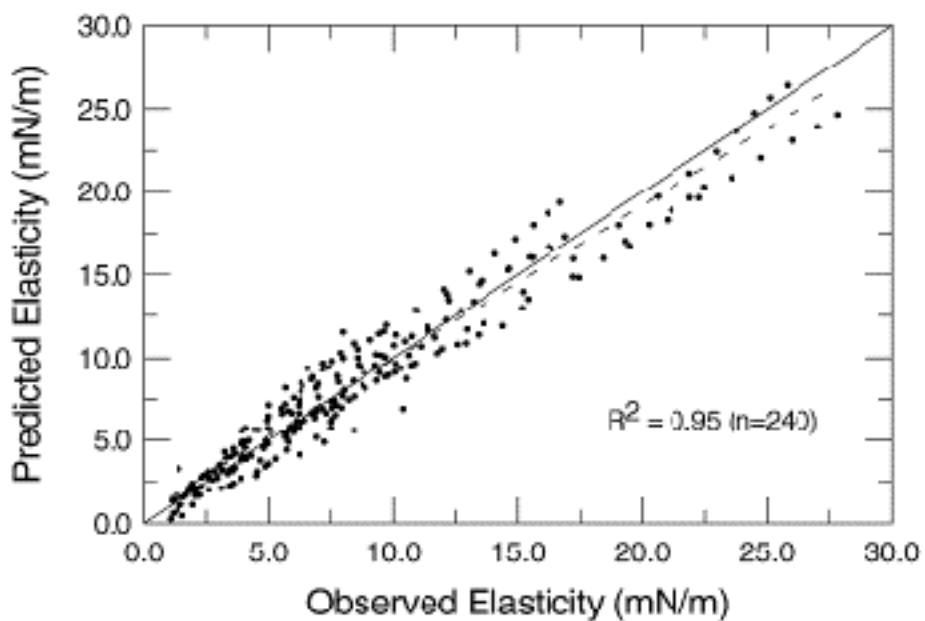


Figure 3. Comparison of Observed Elasticity with Elasticity Predicted from First Discriminant Function D1 Scores Based on Mass Spectral Input for a Suite of 16 Microlayer and Bulk Surface Water Samples from the Mid-Atlantic and Southern California Bights.